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Frontiers of two-dimensional correlation spectroscopy. Part 2. Perturbation methods, fields of applications, and types of analytical probes

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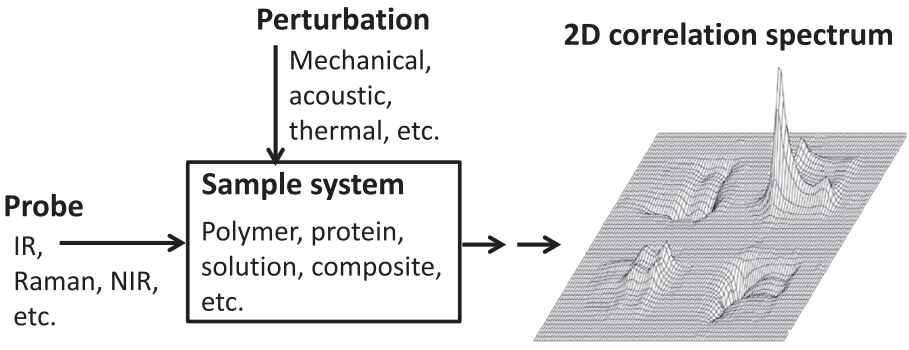
HIGHLIGHTS

- Comprehensive survey on experimental practices in 2D correlation spectroscopy.
- Perturbation methods, fields of applications, and types of analytical probes.
- Physical phenomena, chemical reactions, and biological processes with effects of temperature, concentration, pressure, etc.
- Applications, like polymers, proteins, composites, solution mixtures, etc.
- Probes, like IR, Raman, NIR, fluorescence, NMR, X-ray, Mass spectrometry, etc.

GRAPHICAL ABSTRACT



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ABSTRACT

Noteworthy experimental practices, which are advancing forward the frontiers of the field of two-dimensional (2D) correlation spectroscopy, are reviewed with the focus on various perturbation methods currently practiced to induce spectral changes, pertinent examples of applications in various fields, and types of analytical probes employed. Types of perturbation methods found in the published literature are very diverse, encompassing both dynamic and static effects. Although a sizable portion of publications report the use of dynamic perturbatuions, much greater number of studies employ static effect, especially that of temperature. Fields of applications covered by the literature are also very broad, ranging from fundamental research to practical applications in a number of physical, chemical and biological systems, such as synthetic polymers, composites and biomolecules. Aside from IR spectroscopy, which is the most commonly used tool, many other analytical probes are used in 2D correlation analysis. The ever expanding trend in depth, breadth and versatility of 2D correlation spectroscopy techniques and their broad applications all point to the robust and healthy state of the field.

Abbreviations: ATR, attenuated total reflectance; BSA, bovine serum albumin; DFT, density functional theory; DRIFTS, diffuse reflectance Fourier transform IR spectroscopy; HDPE, high-density polyethylene; IR, infrared; IRRAS, infrared reflection absorption spectroscopy; LCST, lower critical solution temperature; LDPE, low-density polyethylene; LLDPE, linear low density polyethylene; NIR, near infrared; PAS, photoacoustic spectroscopy; PCA, principal component analysis; PCL, polycaprolactone; PEG, polyethylene glycol; PEO, polyethylene oxide; PET, poly(ethylene terephthalate); PHA, poly(3-hydoroxyalkanoate); PHB, poly(3-hydroxybutyrate); PHBHx, poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate); PLA, poly(lactic acid); PLLA, poly(L-lactic acid); PNIPAM, poly(*N*-isopropylacrylamide); PP, polypropylene; PPO, polypropylene oxide; PS, polystyrene; PVME, poly(vinyl methyl ether); ROA, Raman optical activities; STOCSY, statistical total correlation spectroscopy; SAXS, small angle X-ray scattering; SEIRAS, surface-enhanced IR absorption spectroscopy; SERS, surface enhanced Raman spectroscopy; THz, terahertz; UV, ultraviolet; WAXD, wide angle X-ray diffraction; XANES, X-ray adsorption near edge structure; XAS, X-ray absorption spectroscopy; XPS, X-ray photoelectron spectroscopy; 2D, two-dimensional.

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1. Introduction

This survey review was compiled as the second part of the seventh in the series of comprehensive reviews [1–6] to mark the occasion of the Seventh International Symposium on Two-Dimensional Correlation Spectroscopy (2DCOS-7) held in Seoul, Korea in August 2013, covering the period between August 6, 2009 and July 31, 2013. This article is a companion piece for another survey review prepared to cover the new concepts or ideas and emerging developments in the field [7]. Current review focuses on noteworthy experimental practices in the field of two-dimensional (2D) correlation spectroscopy, including the topics of various perturbation methods currently used in 2D correlation spectroscopy experiments, types of analytical probes employed, and pertinent examples of fundamental and practical applications.

2D correlation spectroscopy was originally developed as an obscure mathematical tool to sort out information found in a time-resolved IR linear dichroism spectrum observed for a polymer film undergoing a small-amplitude dynamic deformation [8,9]. The basic idea of treating systematic time-dependent variations of spectral intensities induced by an external perturbation to construct 2D correlation spectra was established at this point. The introduction of the concept of so-called generalized 2D correlation analysis [10–12] dramatically expanded the field 2D correlation spectroscopy. Today, the experimental practices of 2D correlation spectroscopy routinely incorporate the use of various forms of perturbation methods, such as thermal, electrical, and chemical perturbations, application of different types of modern analytical probes, such as IR, Raman, NMR, X-ray, and fluorescence, and both fundamental and applied studies of a vast number of chemical, physical and biological systems [13]. The current survey discusses the itemized topics of recent activities in the field.

2. Dynamic or transient perturbations

A sizable portion of the 2D correlation spectroscopy studies employ dynamic or transient perturbation methods, which induce time-dependent spectral intensity variations reflecting the system response to a perturbation applied to the sample system. Fig. 1 shows the distribution among 113 publications related to time-dependent phenomena studied by 2D correlation spectroscopy. Transient physical processes, such as dynamic response of a sample to mechanical or acoustic stimuli, sorption, diffusion, evaporation and other spontaneous processes, crystallization and other physical phenomena are extensively studied representing about 44% of the literature on dynamic systems. Chemical reactions and kinetics studies, such as polymerization and crosslinking, are also often reported. In the recent years, the number of reports has increased in the 2D correlation spectroscopy study of transient biological processes. Effects of the duration of exposure time to various treatments are also explored here.

2.1. Physical process

2.1.1. Repetitive or pulsed perturbations

In early days, because of the advantage of signal-to-noise ratio gain in cumulative repetitive measurements, 2D correlation spectroscopy experiments often utilized a fixed-frequency sinusoidal perturbation, such as small-amplitude dynamic mechanical deformation and acoustic stimuli, to induce similar sinusoidally varying spectral intensity responses suited for the subsequent 2D correlation analysis [8,9]. Interestingly, there has been rather limited number of such sinusoidal perturbation schemes used in 2D correlation spectroscopy today. Li and Zhang [14] carried out dynamic 2D IR photoacoustic spectroscopy (PAS) study of a layered polymer sample by using a step-scan FT IR spectrometer. Modulated PAS signals were generated by the repetitive fixed-frequency irradiation of IR beam to the sample to achieve the depth profiling of layered materials.

In contrast to the use of a simple sinusoidal perturbation, there have been some activities in the application of multiplexed or pulsed stimuli, which contains more than one frequency component of perturbation effect. Nishikawa et al. [15] reported the 2D correlation spectroscopy based on pulsed compression experiment, which was carried out with a step-scan ATR (attenuated total reflectance) FT IR instrument. In their approach, a series of soft pulses comprising a short duration of mechanical compression with a fixed frequency around microsecond time resolution was used. The resulting IR data were analyzed by the double Fourier transformation along the time axis of mechanical perturbation and the mirror position of the interferometer. This development is particularly significant in the field that it represents the possible emergence of pulse-based 2D correlation spectroscopy outside of NMR or nonlinear optical spectroscopy. Similarly, Rivallan et al. [16] reported the 2D pressure-jump adsorbed species IR technique. The Fourier analysis of time evolution of IR spectrum after sudden pressure change was carried out for the platinum-containing zeolite sample, and different CO oxidation activities were successfully detected for different locations.

2.1.2. Sorption, penetration, diffusion and evaporation

There have been a large number of reports related to the 2D correlation spectroscopy studies of time-dependent spontaneous physical processes which were induced by other than repetitive or pulsed perturbations. Spontaneous sorption, penetration and diffusion of small molecules interacting with host matrices were often studied. For example, Haider et al. [17] reported the 2D ATR-IR study of time-resolved adsorption–desorption spectra to detect the band shift effect, and selective poisoning of colloidal Au catalysis with thiols was explored. Chowdhury [18] used 2D surface enhanced Raman spectroscopy (SERS) to investigate the time-dependent adsorption of 2-aminobenzithiazole onto nano-colloidal silver surface. Le Bihan et al. [19] reported the 2D correlation study of liquid chromatography/mass spectrometry (LC/MS) data obtained for peptide fragments from cytoplasmic proteins. They found fragments with even similar mass and hydrophobicity could be differentiated with 2D correlation by taking advantage of slight difference in elution profiles, suggesting the potential of

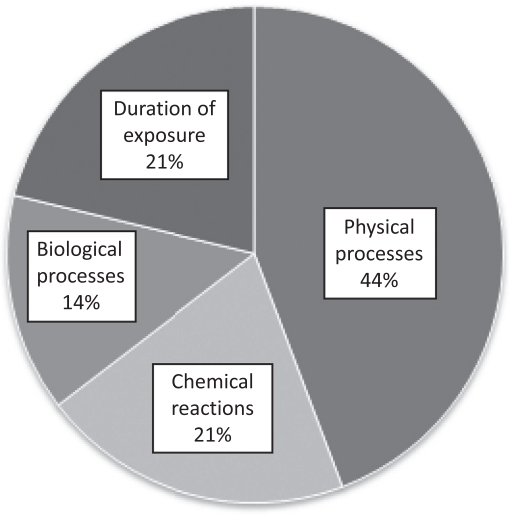

Fig. 1. Time-dependent phenomena studied by 2D correlation spectroscopy.